



# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Gear Lubricant Improving Agents

We, THE LOBRIZOL CORPORATION, of Bucild Station, Cleveland 17, Ohio, United States of America, a corporation duly organized and existing under the laws of the State of Ohio, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to compositions intended for use as lubricants for relatively moving metal surfaces. More particularly, it relates to compositions intended for use as, or for the compounding of, lubricants for the gears of automotive vehicles.

The problems of lubricating automotive gears became increasingly acute during the latter part of the decade 1920—1930, when manufacturers began to replace spiral bevel gears with hypoid gears in the rear axles of automotive equipment.

For reasons inherent in their design, hypoid gears permit the lowering of the center of gravity and the overall height of vehicles. Coupled with these desirable features, however, were many new lubrication problems. It was found that hypoid gears, unlike spiral bevel gears, could not be lubricated satisfactorily with ordinary mineral oils. The great pressures existing between the contacting metal surfaces in hypoid gear systems literally squeezed out the mineral oil lubricant, resulting in metal-to-metal contact under extremely high pressures and subsequent deformation and destruction of the gear surfaces.

Early workers in the lubricant art discovered that destructive metal-to-metal contact in hypoid gear systems could be avoided by the addition of certain oil-soluble chemical compositions to the mineral oil lubricant. These compositions, which were predominantly organic in nature but contained one or more inorganic elements such as sulfur, chlorine, and heavy metal in chemical combination, were believed to react with the gear surfaces under the elevated temperatures which gener-

ally accompany high pressures to form thin films or layers of compounds such as iron sulfide and iron chloride on the gear surfaces. Such films acted as separants and lubricants for the gear surfaces, thereby preventing destructive metal-to-metal contact.

In 1945 two full-scale gear lubricant performance tests were promulgated by the Ordnance Department of the U.S. Army; viz., Specification AXS-1569, "Test Procedure For Determining The Load-Carrying Characteristics of Universal Gear Lubricants Under Conditions Of High Speed," and Specification AXS-1570, "Procedure For Determining The Load-Carrying, Wear, Stability, And Corrosion Characteristics of Universal Gear Lubricants Under Conditions Of High Torque And Low Speed." Although these two tests were originally intended to aid the government and, more particularly, the armed service branches, in purchasing gear lubricants, they were eventually adopted by the petroleum industry at large as criteria for the selection and purchase of gear lubricants destined for the civilian market. For a number of years these tests satisfied the need for tests of good reproducibility which would simulate in the laboratory, insofar as possible, service conditions encountered in actual use of all types of automotive equipment.

However, within recent years, the sharp upward trend of engine horsepower has placed increasingly severe demands upon the hypoid gears which ultimately transmit the engine power to the drive wheels. These demands are not met with a satisfactory margin of safety by currently available gear lubricants which will pass one or both of the Ordnance Department tests referred to above.

From an engineering standpoint, the new service requirement encountered is principally one of greatly increased pressures or loads, particularly those of a sudden or "shock" nature, upon the gear teeth. Since the metallurgy and physical size of the gear has not been altered significantly to accommodate the greater engine torque, the lubricant alone must bear

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the heightened severity of operating conditions if it is to prevent gear failures. This need for a more satisfactory lubricant is particularly critical during the initial "break-in" period of a vehicle, for it is then that the gears are most susceptible to deformation.

As more or less a stop-gap measure, manufacturers of automotive equipment have factory-installed lubricants which will protect the gears against severe shock loading, even though such lubricants have been shown to be of little or no value in protecting the gears under service conditions including high torque and low speed.

The problem of providing a gear lubricant which will lubricate hypoid gears in a changing operating environment wherein shock load, high speed, and high torque demands are made both cyclically and in sequence on the lubricant is a very difficult one. The difficulty stems principally from the fact, well known to workers in the lubricant art, that materials which help the lubricant perform its task under one set of operating conditions, say shock loading at high speeds, generally reduce or, in some instances, even nullify the effect of materials added to improve the performance of the lubricant under a different set of operating conditions; e.g., high torque loading at relatively lower speeds.

By effecting a critical balance between the proportions of materials known to be effective under (a) high speed operating conditions, and (b) high torque relatively lower speed operating conditions, other workers in the lubricant art have been able to produce lubricants which meet the requirements of the aforesaid Army Ordinance high speed and high torque performance tests.

All of such carefully balanced or "compromise" lubricants have not proved amenable to modification, however, so as to enable them to withstand both severe shock loads at high speeds and high torque loads at relatively lower speeds. The addition thereto of materials known to be effective under shock load conditions upsets the carefully balanced lubricant and renders it substantially less effective in a high torque-low speed operating environment.

It has now been discovered that lubricants which contain certain critical proportions of both (a) an oil-soluble phosphorodithioic acid diester derivative of the type described below, and (b) an oil-soluble organic polysulfide of the type described below perform very satisfactorily in the hypoid gear systems of modern, high-powered automotive equipment under severe operating conditions characterized by shock load, high speed, and high torque demands.

In accordance with the present invention, there is provided a composition comprising

(A) an oil-soluble derivative of a phosphorodithioic acid diester selected from phos-

phorodithioic acid triesters, metal salts of phosphorodithioic acid diesters, bis(phosphorodithioic acid) tetraesters, and phosphorodithioic acid diester thioanhydrides; and

(B) an oil-soluble turpentine or oil-(aralkyl) polysulfide each molecule of which has at least one sulfur atom bonded only by secondary valency bonds;

components A and B being present in relative proportions such that a solution containing from 3.5 to 15 weight per cent. of a mixture of the two components contains

(i) from 0.20 to 0.75, preferably 0.3 to 0.5, weight percent of phosphorus; and

(ii) from 0.25 to 1.0, preferably 0.5 to 0.9, weight per cent. of chemically combined sulfur bonded only by secondary valency bonds. The relative proportion of phosphorus to sulfur which is bonded only by secondary valency bonds will preferably be within the range of from about 1:1 to about 1:2. Component A may desirably be a phosphorodithioic acid triester in which one of the ester radicals contains an inorganic substituent. This radical may be, for example, an aliphatic radical and the inorganic substituent may be hydroxy.

In addition to the two characterizing components A and B, the lubricant improving agent and lubricants compounded from it may also contain, if desired, auxiliary improving agents such as, for example, rust inhibitors, oiliness agents, and viscosity index improvers. The presence of these and other auxiliary agents, however desirable they may be for their contribution to the qualities of the finished lubricant, is not required to prevent gear deformation under severe operating conditions.

#### COMPONENT A:

The Oil-Soluble Substituted Phosphorodithioic Acid Containing An Organic Substituent.

Materials useful as this component are derivatives of phosphorodithioic acid di-esters and may be defined by the following formula:



where  $R_1$  and  $R_2$  are the same or different organic radicals and X is the hydrogen equivalent of a radical or atom capable of chemically replacing the acidic hydrogen atom of the phosphorodithioic acid di-ester and is selected from the class consisting of organic radicals and metal atoms.

In the formula given above for Component A,  $R_1$  and  $R_2$  are the same or different aromatic, aliphatic, or cycloaliphatic radicals, which radicals may be hydrocarbon in nature or contain substituents such as, e.g., chloro, bromo, fluoro, nitro, alkoxy, thioalkoxy and

carboalkoxy.  $R_1$  and  $R_2$  are usually hydrocarbon radicals such as; e.g., aryl, alkaryl, aralkyl, cycloalkyl, and straight- or branched-chain alkyl radicals. They are preferably alkyl radicals containing from 1 to about 40 carbon atoms such as; e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, n-amyl, isomyl, n-hexyl, 4-methyl-2-pentyl, n-octyl, capryl, n-nonyl, 3,5,5-trimethyl-hexyl, dodecyl, hexadecyl, eicosyl, tricosyl, and alkyl radicals or from about 20 to 40 carbon atoms derived from petroleum waxes.

As indicated earlier,  $R_1$  and  $R_2$  may be different. A particularly valuable class of phosphorodithioic acid di-esters useful as starting materials for the preparation of Component A are those in which (1)  $R_1$  and  $R_2$  are different alkyl radicals, one containing at least 6 carbon atoms and the other containing less than 6 carbon atoms; or (2) at least two different phosphorodithioic acid di-esters are present,  $R_1$  and  $R_2$  of one acid being alkyl radicals of at least 6 carbon atoms each and  $R_1$  and  $R_2$  of a second acid being alkyl radicals of less than 6 carbon atoms each.

$X$ , as indicated above, is a radical or atom capable of chemically replacing the acid hydrogen atom of the phosphorodithioic acid di-ester and selected from the class consisting of organic radicals and metal atoms. By the latter statement it is not meant to infer that all organic radicals and/or metal atoms are fully equivalent for the purposes of this invention, since some are preferred over others for certain uses.

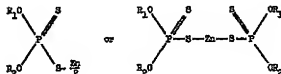
Where  $X$  is an organic radical, it is preferably an organic radical containing at least one inorganic element or substituent. More particularly, it is an aromatic or aliphatic radical and preferably an aliphatic radical containing at least one inorganic element such as; e.g., oxygen, sulfur, phosphorus, halogen, nitrogen,

and metal. Among the inorganic-substituted aliphatic radicals most suitable as  $X$  are (1) hydroxyl-substituted aliphatic radicals, and (2) aliphatic radicals containing at least two different inorganic elements such as; e.g., phosphorus and sulfur-substituted aliphatic radicals and metal-and-oxygen-substituted aliphatic radicals.

In this group of inorganic substituted aliphatic radicals most suitable as  $X$ , a preference exists for monohydroxyalkyl radicals and the anionic radicals of phosphorodithioic acid di-esters.

Thus  $X$  may be, for example, one of the following radicals: 2-chloroethyl, 2-hydroxyethyl, 2- and 3-hydroxypropyl, 2-mercaptoethyl, 2- and 3-mercaptopropyl, 4-nitrobutyl, 3-hydroxybutyl, 2-cyanopropyl, trichloromethyl, 4-chlorobenzyl, trichlorobenzyl, 2-methyl-4-oxo-2-pentyl, heptyl, capryl, 4-oxocyclohexyl, 2-thio-butyl, the anionic radical of di-(4-methyl-2-pentyl) phosphorodithioic acid, the anionic radical of di-(methyl-cyclohexyl) phosphorodithioic acid, carbamethoxymethyl, carbomethoxyethyl, hydroxyethoxymethyl, epoxypropyl, 2,4-dihydroxybutyl, carbomethoxymethyl, zinc carbomethoxymethyl, and lead-carboxyethyl.

When  $X$  is a metal atom, the metal is usually polyvalent and preferably a heavy metal of atomic weight greater than 50 such as; e.g., zinc, cadmium, barium, strontium, lead, or tin, with a particular preference for zinc. It is to be understood that in the case of an atom of a polyvalent metal which atoms contain two or more equivalents of metal, the additional valence bonds of the metal will extend similarly to anions of the phosphorodithioic acid di-ester. Thus, for example a zinc salt of a phosphorodithioic acid di-ester can be represented by either of the structures below:



wherein  $Zn$  and  $Zn$  represent, respectively, one hydrogen equivalent and two hydrogen equivalents of zinc.

Specific examples of materials useful as Component A are as follows, which examples are presented for purposes of illustration only and are not to be construed as limiting the scope of the invention:

Phosphorodithioic acid tri-esters such as, e.g.:

Diethyl 2-chloroethyl phosphorodithioate

Di-isopropyl 2-hydroxypropyl phosphorodithioate

Di-isopropyl 3-hydroxypropyl phosphorodithioate

Di-sec-butyl 2-mercaptopropyl phosphorodithioate

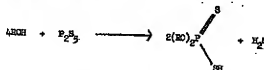
Di-n-pentyl 4-nitrobutyl phosphorodithioate

Di-(4-methyl-2-pentyl) 2-hydroxypropyl phosphorodithioate

Di-(4-methyl-2-pentyl) 3-hydroxypropyl phosphorodithioate

Di-isopropyl heptyl phosphorodithioate

- Di-n-hexyl capryl phosphorodithioate  
Di-nonyl hydroxyethoxyethyl phosphorodithioate  
Di-lauryl 3-hydroxybutyl phosphorodithioate  
Di-(2-ethyl-hexyl) 2-hydroxypropyl phosphorodithioate  
Di-(2-ethyl-hexyl) carbomethoxyethyl phosphorodithioate  
Di-(4-methyl-2-pentyl) carbomethoxyethyl phosphorodithioate  
Di-(4-methyl-2-pentyl) carbomethoxyethyl phosphorodithioate  
Di-(4-methyl-2-pentyl) 2-cyanoethyl phosphorodithioate  
Di-(4-methyl-2-pentyl) 2-methyl-4-oxo-2-pentyl phosphorodithioate  
Di-(4-tert-butyl-phenyl) 2-hydroxy-ethyl phosphorodithioate  
Di-(4-tert-butyl-phenyl) 3-hydroxy-pentyl phosphorodithioate  
Di-benzyl 2-mercaptoethyl phosphorodithioate  
Di-(2-phenethyl) trichloromethyl phosphorodithioate  
Di-(2-ethyl-hexyl) zinc-carboxymethyl phosphorodithioate  
Di-(2-ethyl-hexyl) lead-carboxyethyl phosphorodithioate  
Bis-phosphorodithioates such as, e.g., bis-(di-alkyl phosphorodithioates):  
Bis-[di-(4-methyl-2-pentyl) phosphorodithioate]  
Bis-[di-(methyl-cyclohexyl) phosphorodithioate]  
Phosphorodithioic acid di-ester thioanhydrides such as, e.g.:  
Thioanhydride of di-n-butyl phosphorodithioic acid  
Metal salts of phosphorodithioic acid di-esters such as, e.g.:  
Zinc di-(4-methyl-2-pentyl) phosphorodithioate  
Zinc di-organo phosphorodithioate made by neutralizing a mixture of 40 mole-percent of di-isopropyl phosphorodithioic acid and 60 mole-percent of di-(4-methyl-2-pentyl) phosphorodithioic acid, with zinc oxide  
Zinc di-isopropyl 4-methyl-2-pentyl phosphorodithioate  
Zinc di-(3,5,5-trimethyl-hexyl) phosphorodithioate  
Zinc n-butyl 4-methyl-2-pentyl phosphorodithioate  
Zinc di-lauryl phosphorodithioate  
Zinc di-(tert-octyl-phenyl) phosphorodithioate  
Lead di-capryl phosphorodithioate  
Stannous di-ethyl phosphorodithioate  
Cadmium di-cycetyl phosphorodithioate  
Barium di-lauryl phosphorodithioate
- From the foregoing it will be noted that materials of particular utility as Component A are derivatives of phosphorodithioic acid di-esters selected from the class consisting of tri-esters, metal salts, and bis-phosphorodithioates thereof. Of this group, a preference exists for the zinc salts of phosphorodithioic acid di-esters, with a special preference for zinc salts of di-alkyl esters of phosphorodithioic acid. An eminently suitable group of such zinc salts of di-alkyl esters of phosphorodithioic acid are those in the molecular structure of which there is present a substantial proportion of each of (a) alkyl radicals containing at least 6 carbon atoms, and (b) alkyl radicals containing less than 6 carbon atoms.
- The preparation of compounds useful as Component A is well-known in the art. In most instances, the starting material will be a phosphorodithioic acid di-ester produced by the reaction of an organic hydroxy body with phosphorus pentasulfide according to the following equation, in which R represents an aliphatic, cycloaliphatic, or aromatic substituent preferably alkyl (particularly lower alkyl) or aryl:



- From the phosphorodithioic acid di-ester may then be derived by known processes the Component A of the present invention. In the interest of not unduly lengthening the present specification, reference may be made to the following U.S. Patents, which disclose methods for the preparation of materials useful as Component A:
- 1,889,943; 1,949,629; 2,063,629; 2,198,915; 2,261,047; 2,266,514; 2,329,436; 2,342,572; 2,343,213; 2,343,831; 2,344,392; 2,344,393; 2,344,395; 2,347,592; 2,365,938; 2,368,000; 2,372,358; 2,494,126; 2,494,283; 2,494,284; 2,528,732; 2,529,304; 2,540,084; 2,561,773;
- 2,565,920; 2,578,652; 2,586,655; 2,586,656; 2,611,728; 2,611,729; 2,632,020; 2,645,657; and 2,659,705.
- COMPONENT B:  
The Oil-Soluble Turpentine or Di-alkyl Polysulfide having at least one Sulfur Atom bonded only by Secondary Valence Bonds.
- In these disulfides, the turpentine or alkyl radicals may be hydrocarbon in nature or contain substituents such as, e.g., chloro-, fluoro-, bromo-, alkoxy-, carbalkoxy-, nitro-, nitroso-, and hydroxyl. In most instances they are hydrocarbon radicals but for some uses the presence

of organic or inorganic substituents is desirable. The radicals may be, for example, benzyl, chlorobenzyl, or dichlorobenzyl. Other chlorine-substituted benzyl radicals are also suitable, the position of the substituent or substituents being immaterial. The sulfide part of the molecule contains at least 2 and generally not more than 7 sulfur atoms. More desirably it contains at least 3 and not more than 6, preferably at least 4 and not more than 5, sulfur atoms. In certain instances, as in the case of mixed organic polysulfides, the number may be non-integral such as 3.3 or 4.6. For example, an equimolar mixture of an organic tetrasulfide and an organic trisulfide would provide an average number of 3.5 sulfur atoms in the molecule.

By the phrase "sulfur atom bonded only by secondary valency bonds" we mean a sulfur atom which is bonded only to one or more sulfur atoms in the polysulfide molecule and is thus devoid of valency bonds extending to the organic radicals in the polysulfide molecule. The exact nature of such secondary valency bonds is not clearly understood, but it is known that they are much weaker than the covalent bond which exists between a sulfur atom and a carbon atom of an organic radical in an organic polysulfide.

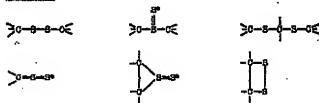
Due to the relatively weak attachment of sulfur atoms which are bonded only by secondary valency bonds, such sulfur is more

readily given up by the molecule; i.e., is more reactive chemically, than sulfur which is bonded to a carbon atom of an organic radical. The very fact that such sulfur is chemically reactive facilitates its determination. For example, a test sample of the organic polysulfide may be treated with reagents which are known to react with and thus to remove reactive sulfur such as, e.g., warm aqueous solutions of caustic alkali, warm aqueous solutions of metallic monosulfides, and finely divided metals such as copper, lead, iron, and silver. The loss in sulfur content of the test sample of organic polysulfide after such treatment corresponds to the amount of reactive sulfur originally present; i.e., that sulfur which is bonded only by secondary valency bonds.

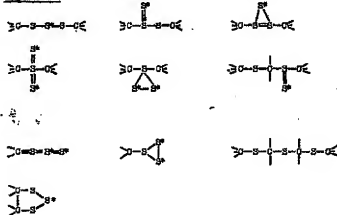
Thus it is possible to characterize an organic polysulfide both by its content of (a) "total sulfur"; i.e., sulfur in all forms, and (b) sulfur bonded only by secondary valency bonds. The discovery that certain critical amounts of the kind of sulfur indicated in (b) must be present in our lubricants constitutes one of the principal features of our invention.

The following partial structures illustrate some of the many arrangements which sulfur atoms can assume in organic polysulfides. In each of these partial structures the presence of an asterisk next to a sulfur atom indicates that such sulfur atom is held in the molecule by secondary valency bonds only:

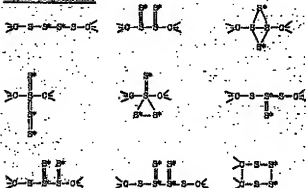
#### Disulfides



#### Trisulfides



## Higher polysulfides



From a study of the structures given above, it will be apparent that organic polysulfides of like molecular weight and containing the same percentages of chemical elements may possess widely different amounts of reactive sulfur depending on the mode of attachment of the sulfur atoms within the molecule. Those structures which possess the largest number of sulfur atoms bonded only by secondary valency bonds will possess the highest percentage of reactive sulfur.

Specific examples of organic polysulfides which contain at least one sulfur atom bonded only by secondary valency bonds and which are useful as Component B in lubricants of this invention are, for example:

- Di-benzyl trisulfide
- Di-benzyl tetrasulfide
- Di-benzyl polysulfides containing an average of 4.6 sulfur atoms per molecule
- Di-benzyl pentasulfide
- Di-benzyl hexasulfide
- Monochloro di-benzyl tetrasulfide (i.e., benzyl monochlorobenzyl tetrasulfide)
- Di-(5-chlorobenzyl) tetrasulfide
- Di-(2,4-dichlorobenzyl) tetrasulfide
- Di-phenethyl tetrasulfide

Turpentine polysulfides containing an average of 2.6 sulfur atoms per molecule.

The preparation of materials useful as Component B may be accomplished by any of the many different processes which are known and disclosed in the art including, for example, the reaction of halogen-bearing organic compounds with alkali metal polysulfides, the reaction of mercaptans with sulfur and/or sulfur halides, the reaction of saturated and unsaturated hydrocarbons with sulfur and/or sulfur halides, and the reaction of organic monosulfides with sulfur.

## AUXILIARY IMPROVING AGENTS

As previously indicated, there may also be present in our lubricants certain auxiliary improving agents such as, for example, detergents, rust-preventatives, film strength

agents such as halogenated organic compounds, oiliness agents such as fatty oils and sulfurized fatty oils, pour point depressors, foam inhibitors, viscosity index improvers, oxidation inhibitors, and odor improvers. Included among the many materials useful for these various purposes are the following:

Detergents such as metal salts of petroleum naphthenic acids, petroleum sulfonic acids, and the higher fatty acids; rust-preventatives such as basic metal petroleum sulfonates, metal phenolates, organic amines, and benzyl thiocyanate; film strength agents such as chlorinated paraffin waxes containing from 20 to 70% chlorine, chlorinated zirconium containing from 50 to 60% chlorine, hexachloro-diphenyl ether, and polychlorobiphenyl; oiliness agents such as olefin, methyl oleate, oleic acid, sulfurized and non-sulfurized sperm oil, and coen oil; pour point depressors such as wax-alkylated naphthalene or phenanthrene; foam inhibitors such as the polymeric di-alkyl siloxanes; and viscosity index improvers such as polymerized and co-polymerized alkyl methacrylates, and polymerized butylenes.

It is understood, however, that the use of any of such auxiliary agents is optional and not required in our lubricants to prevent the deformation of gear surfaces.

## THE OIL BASE

The lubricating oil base in which the characterizing Components A and B of this invention and any desired auxiliary agents are incorporated may be of synthetic, vegetable, animal, or mineral origin. Because of their low cost, availability, and desirability, the mineral oils; i.e., those derived from petroleum, find the widest application in the lubricant art.

There are at the present time sundry mineral oils, each best suited from the standpoint of viscosity and other properties for different climates and operating environments. The oil base of a lubricating composition of the present invention will preferably comprise a mineral lubricating oil having characteristics

now well recognized as best suited for such environment and climate.

In Table I following, the characteristics of mineral lubricating oils best suited for a given environment and climate are disclosed. The

actual upper limit of preferred viscosity index is infinite for most uses. The values given in the table for viscosity index represent current commercial maximum values.

TABLE I

Type of climate	Application in:	
	Automotive gears	Industrial gears
<b>Arctic:</b>		
Preferred viscosity range <sup>1</sup>	30—80/210° F.	30—1000/210° F.
Flash point preferably no lower than	300° F.	300° F.
Pour point preferably no higher than	—30° F.	10° F.
<b>Temperate:</b>		
Preferred viscosity range <sup>1</sup>	50—140/210° F.	50—2000/210° F.
Flash point preferably no lower than	325° F.	325° F.
Pour point preferably no higher than	0° F.	20° F.
<b>Tropical:</b>		
Preferred viscosity range <sup>1</sup>	80—200/210° F.	80—2000/210° F.
Flash point preferably no lower than	350° F.	325° F.
Pour point preferably no lower than	20° F.	30° F.
Preferred viscosity index for all climates (Dean and Davis scale)	75—150	35—120

<sup>1</sup> Expressed in Saybolt Universal seconds at the indicated temperature.

#### LUBRICANTS AND LUBRICANT IMPROVING AGENTS

As indicated previously, a number of hypoid gear lubricants representative of the several fundamental types which are commercially available were first investigated to determine their effectiveness in preventing deformation of gear surfaces in an operating environment characterized by severe "shock" loads at high speeds and high torque loads at relatively lower speeds.

Full-scale performance tests, i.e., tests using standard automotive equipment, employed in this connection included the United States Army Ordnance AXS-1569 high speed and

AXS-1570 high torque tests and, in addition, a new severe shock test using a 1953 model "Buick" passenger car equipped with a torque converter transmission of the "Dynaflow" variety. ("Buick" is a registered trade mark).

The latter test, termed for convenience the "Buick Shock Test," is one of almost unbelievable severity. It is carried out in the laboratory by mounting the rear drive wheels of the car on a heavy shaft which is free to revolve and which is designed to simulate the inertia of the car on a level highway. Although the test could conceivably be conducted on the open road, the severe operating conditions

specified in its procedure would make such a course extremely hazardous.

In carrying out the test, the rear axle of the car is filled to the specified level with the desired test lubricant and the car is run for the equivalent of 19 miles at 40-50 m.p.h. to break in the new gears. The car is then accelerated from 0 to 70 m.p.h. and decelerated to 0 m.p.h. with the transmission in drive position. If no unusual noise is detected in the rear axle, the car is subjected to a high speed evaluation comprising 10 cycles of acceleration and deceleration, 0 to 70 to 0 m.p.h., with the transmission in drive position.

Next, for the shock portion of the test, the car brakes are applied, the throttle opened with the transmission in low position, and the brakes released suddenly. When the car reaches 30 m.p.h. the transmission is shifted to the drive position and acceleration is continued to 75 m.p.h. The throttle is then closed and the car is decelerated to 65 m.p.h., at which speed the transmission is shifted abruptly to the low position. From the preceding description, it is apparent to one familiar with automotive equipment that shock loads of extreme severity

are placed upon the coast and drive surfaces of the hypoid gear teeth.

After the shock portion of the test is completed, the high speed evaluation described earlier and comprising 10 cycles of acceleration and deceleration is repeated.

The car is stopped and the pinion and ring gears are removed and inspected for evidence of deformation such as rimping, ridging, spalling, and scoring. These terms define certain specific kinds of deformation which are readily distinguished from each other by trained mechanics. If such inspection shows the gear teeth to be free from deformation, the lubricant is said to have passed the test.

Table II includes the results obtained on commercially available hypoid gear lubricants in the three full-scale tests which have been described. The lubricants are defined by chemical type in terms which are familiar to those in the lubricant art. It will be noted that none of the lubricants gave satisfactory performance in all of the tests, even though several satisfied the less rigorous requirements of the two well-known Army Ordnance tests.

TABLE II

Type of lubricant	Test Result		
	Buick Shock	High Speed AXS-1569	High Torque AXS-1570
Lead soap-oxidative sulfur	Pass	Pass	Fail
Chlorine-mild sulfur-phosphorus (regular duty)	Fail	Pass	Pass
Chlorine-mild sulfur-phosphorus (heavy duty)	Fail	Pass	Pass
Chlorine-mild sulfur	Fail	Pass	Fail
Fixed oil-mild sulfur	Fail	Pass	Fail

These results point to the critical situation which preceded the present discovery, viz., that no hypoid gear lubricant was available which would withstand both the rigors of shock loads at high speeds and high torque loads at relatively lower speeds.

As stated hereinbefore, lubricants capable of giving satisfactory performance under these extremes of operating conditions can be made by incorporating therein certain critical proportions of two characterizing components; viz., (A) an oil-soluble phosphorodithioic acid diester derivative of the type described, and (B) an oil-soluble organic polysulfide of the type described having at least one sulfur atom bonded only by secondary valency bonds.

Table III includes test data on many lubricants containing the characterizing com-

ponents A and B of the present invention in amounts which either come within or fall outside of the ranges found to be critical for each.

The tests employed were the Buick Shock test, the Army Ordnance AXS-1570 high torque test, and the SAB Extreme-Pressure Lubricant test at 1000 r.p.m. Army Ordnance test AXS-1569 was not employed in these studies since it had been determined that any lubricant which passed the Buick Shock test, which test includes a high speed evaluation, would always pass the less severe AXS-1569 test.

The SAB Extreme-Pressure Lubricant test included in Table III is a test which is well-known in the lubricant art. It is carried out on the SAB Lubricant machine in the manner set forth in J. Inst. Petroleum, April 1946,



pages 225-226. It was found that lubricants that failed this test, would also fail in the full 590-690 rpm test, and would fail the Buick Shock test. Since it was not feasible to conduct Buick Shock tests on all of the large number of lubricants investigated, the SAB test was employed to screen out lubricants which would not pass the former test.

It will be noted that in every instance when one or both of the two characterizing components A and B was present in an emulsion, failing the full 590-690 rpm test, the Buick Shock test, the lubricant failed to give satisfactory performance. On the other hand, when these same components were each present in a lubricant in amounts within the range found

to be operative, the lubricant was effective in preventing gear deterioration under both shock loads at high speeds and high torque loads at low speeds. It is apparent, by conventional definition, that the foregoing compositions of the invention in Table III have been indicated by an asterisk (\*).

TABLE III

All percentages of improving agents are by weight based on the total lubricant

#### Component A materials employed:

- A-1 = zinc di-orthophosphorodithioate made by neutralizing a mixture of 40 mole-percent of  $O_2O$ -di-*isopropyl* phosphorodithioic acid and 60 mole-percent of  $O_2O$ -di-(4-methyl-2-pentyl) phosphorodithioic acid with zinc oxide
- A-2 = zinc  $O_2O$ -di-(4-methyl-2-pentyl) phosphorodithioate
- A-3 =  $O_2O$ -di-(4-methyl-2-pentyl) hydroxypropyl phosphorodithioate
- A-4 = Bis-( $O_2O$ -di-(4-methyl-2-pentyl) phosphorodithioate)

#### Component B materials employed:

- B-1 = monochlor dibenzyl tetrasulfide (a mixture of *o*, *m*- and *p*-isomers)
- B-2 = di-benzyl polysulfides containing an average of 4.6 sulfur atoms per molecule
- B-3 = turpentine polysulfides containing an average of 2.6 sulfur atoms per molecule

TABLE III—continued.  
SAE 90 grade gear lubricant (mineral lubricating oil) containing the indicated kind and amounts of improving agents:

Lubricant No.	Component A			Component B			Test
	Kind	%	% P contributed to lubr.	Kind	%	% sec. S contributed to lubr.	
1	none	—	—	B-1	5.22	0.97	Pass
2	A-1	6.7	0.71	none	—	—	Fail
3	A-1	1.07	0.11	B-1	3.75	0.70	Fail
4	A-1	4.78	0.51	B-1	0.84	0.16	Fail
5*	A-1	3.5	0.37	B-1	2.84	0.53	Pass
6	A-2	4.4	0.42	none	—	—	Fail
7	A-2	0.87	0.082	B-2	2.85	0.71	Fail
8	A-2	1.57	0.15	B-2	4.28	1.07	Pass
9	A-2	3.47	0.33	B-2	0.71	0.18	Fail
10*	A-2	3.78	0.36	B-2	2.34	0.59	Pass
11*	A-2	4.4	0.42	B-2	2.05	0.51	Pass
12*	A-2	5.37	0.51	B-2	3.33	0.83	Pass
13*	A-2	4.4	0.42	B-3	3.64	0.85	Pass
14*	A-3	5.25	0.42	B-2	2.73	0.68	Pass
15*	A-4	3.94	0.37	B-2	2.73	0.68	Pass

\* "sec. S" = % sulfur bonded only by secondary valency bonds

Additional examples of lubricants containing additives of the invention are disclosed in Table IV. These are presented for purposes of illustration only and are not to be construed as limiting the scope of the invention, particularly with respect to the inclusion of optional auxiliary improving agents such as, e.g., detergents, oiliness agents, and foam inhibitors.

The numerical values in parentheses, e.g., (0.37% F) and (0.5% sec. S), following the characterizing Components A and B indicate, respectively, the percent phosphorus and percent sulfur bonded only by secondary valency bonds imparted to the finished lubricant by the particular component. The SAE 80 and SAE 90 gear lubricants are mineral lubricating oils.

TABLE IV

Lubricant No.	% By Weight	Composition
16	89.17	SAE 90 gear lubricant
	4.4	zinc O,O-di-(4-methyl-2-pentyl)phosphorodithioate (0.42% F)
	2.73	di-benzyl polysulfides containing an average of 4.6 sulfur atoms per molecule (0.68% sec. S)
	0.4	lead naphthenate
	3.3	chlorinated eicosane containing 50% chlorine
17	87.57	SAE 90 gear lubricant
	4.4	zinc O,O-di-(4-methyl-2-pentyl) phosphorodithioate (0.42% F)
	2.73	di-benzyl polysulfides containing an average of 4.6 sulfur atoms per molecule (0.68% sec. S)
	2.0	sulfurized sperm oil
	3.3	chlorinated eicosane containing 50% chlorine
18	90.3	SAE 90 gear lubricant
	5.5	O,O-di-(4-methyl-2-pentyl) 2-hydroxyethyl phosphorodithioate (0.5% F)
	3.7	di-phenethyl tetrasulfide (0.7% sec. S)
	0.5	basic calcium petroleum sulfonate

- 20 It is common practice in the lubricant additive industry to provide a liquid, homogeneous improving agent concentrate containing high percentages of one or more separate improving agents and, optionally, a proportion of a mineral oil, preferably one of low viscosity. Such concentrates dissolve readily in lubricating oil bases and minimize the problems associated with handling, storage, and transportation. A further benefit in cases where two or more separate improving agents are to be incorporated in the oil base is that the relative proportions of the several improving agents can be

adjusted within the concentrate by the manufacturer. Then in preparing the finished lubricant, a single addition of only one concentrate need be made to the oil base to impart thereto the desired improving agents in predetermined relative proportions.

Concentrates intended for compounding with an oil base to yield lubricants of the present invention will always contain the two previously identified characterizing Components A and B and optionally:

- (1) certain desired auxiliary improving agents; and

(2) a proportion, generally from about 10% to about 70% by weight based on the total concentrate, of a low-viscosity mineral oil.

Depending on the particular Components A and B employed, the presence of auxiliary improving agents, and, in some instances, the presence of mineral oil in the concentrate, the amount thereof required to impart to the lubricant the necessary percoat phosphorus and percent sulfur bonded only by secondary valency bonds will vary considerably within the limits stated. Generally an amount of the concentrate equal to from about 3.5% by about 15% based on the weight of the total lubricant will be suitable.

WHAT WE CLAIM IS:

1. A composition comprising

(A) an oil-soluble derivative of a phosphorodithioic acid diester selected from phosphorodithioic acid triesters, metal salts of phosphorodithioic acid diesters, bis(phosphorodithioic acid) tetraesters, and phosphorodithioic acid diester thioanhydrides; and

(B) an oil-soluble turpentine or di-(aralkyl) polysulfide each molecule of which has at least one sulfur atom bonded only by secondary valency bonds;

components A and B being present in relative proportions such that a solution containing from 3.5 to 15 weight per cent of a mixture of the two components contains

(i) from 0.20 to 0.75 weight per cent of phosphorus; and

(ii) from 0.25 to 1.0 weight per cent of chemically combined sulfur bonded only by secondary valency bonds.

2. A composition as claimed in claim 1, in which components A and B are present in such proportions that a solution containing from 3.5 to 15 weight per cent of a mixture of the two components contains

(i) from 0.3 to 0.5 weight per cent of phosphorus; and

(ii) from 0.5 to 0.9 weight per cent of chemically combined sulfur bonded only by secondary valency bonds.

3. A composition as claimed in claim 1 or 2, in which the relative proportion of phosphorus to sulfur which is bonded only by secondary valency bonds is within the range of from about 1:1 to about 1:2.

4. A composition as claimed in any one of claims 1-3 in which Component A is a derivative of a di-alkyl ester of phosphorodithioic acid in which one alkyl group contains at least 6 carbon atoms and the other alkyl group contains fewer than 6 carbon atoms.

5. A composition as claimed in any one of

claims 1-4 in which Component A is a salt of a di-alkyl ester of phosphorodithioic acid in the molecular structure of which there is present a substantial proportion of each of (a) alkyl radicals containing at least 6 carbon atoms, and (b) alkyl radicals containing fewer than 6 carbon atoms.

6. A composition as claimed in any one of claims 1-4 in which Component A is a polyvalent-metal salt of a phosphorodithioic acid di-ester.

7. A composition as claimed in claim 6 in which the metal is a heavy metal having an atomic weight greater than 50.

8. A composition as claimed in claim 7 in which the metal is zinc.

9. A composition as claimed in any one of claims 1-4 in which Component A is a phosphorodithioic acid tri-ester in which one of the ester radicals contains an inorganic substituent.

10. A composition as claimed in claim 9 in which Component A is a phosphorodithioic acid tri-ester in which one of the ester radicals is an inorganic substituted aliphatic radical.

11. A composition as claimed in claim 10 in which Component A is a phosphorodithioic acid tri-ester in which one of the ester radicals is a hydroxy-substituted aliphatic radical.

12. A composition as claimed in claim 11, in which Component A is a phosphorodithioic acid tri-ester in which one of the ester radicals is a mono-hydroxyalkyl radical.

13. A composition as claimed in any one of claims 1-4 in which Component A is a bis-(di-alkyl phosphorodithioate).

14. A composition as claimed in any one of claims 1-13 in which Component B contains at least 2 and not more than 7 sulfur atoms.

15. A composition as claimed in claim 14 in which Component B contains at least 3 and not more than 6 sulfur atoms.

16. A composition as claimed in any one of claims 1-15 in which Component B is a di-benzyl polysulfide.

17. A composition as claimed in claim 16 in which Component B is a mixed di-benzyl polysulfide containing an average of from 4 to 5 sulfur atoms.

18. A composition as claimed in claim 16 or 17 in which Component B is a chlorine-substituted di-benzyl polysulfide.

19. A composition as claimed in claim 1, in which Components A and B are selected from those set forth in the descriptive part of the specification.

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